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(54) **Pressurised roller pens and inks for such pens**

(57) A pressurized roller pen includes a thixotropic viscoelastic ink that is a gel at rest, but becomes a thin liquid under the shearing action of the pen's revolving ball-point, and comprises at least one polyelectrolyte polymer, at least one highly polar solvent, at least one solvent of low or medium polarity, and colloidal silica, together with pigments, dyes, surfactants and/or pH modifiers.

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SPECIFICATION

Pressurised roller pens and inks for such pens

Ball-point pens containing low viscosity inks have been commercially available since 1948. Because they write easily with little pressure and produce intense, opaque lines, they have attained commercial acceptance. Manufacturing such pens to uniform quality standards is difficult, however, for these reasons: (1) because their ink reservoirs are open to the atmosphere, their inks tend to evaporate, reducing shelf life; (2) because capillary action feeds ink to the ball of such pens, any break in the capillary ink channels from the reservoir to the ball of such pens causes them to stop writing; (3) sometimes, inks flow too rapidly from their reservoirs causing excessive ink to accumulate on the point of the pens; and (4) the absorbent felt-type ink reservoirs in these pens have small capacities.

Our new pressurized ball-point roller pens with their new inks overcome these problems. Because our ink cartridges are sealed, the inks cannot evaporate or dry out. Because our ink cartridges are pressurized, the inks feed dependably without requiring capillary action. Because our inks are gels while at rest, and because our inks are highly adhesive and viscoelastic, our inks do not ooze, and excessive ink seldom accumulates around the ball tip. Because our ink reservoirs are sealed and pressurized, they can hold a large quantity of usable ink.

Our invention provides pressurized ball-point roller pens that write more easily than other pressurized ball-point pens and almost as easily as unpressurized roller pens. The new inks form gel structures at rest, but become thin liquids that flow easily, yet adhere to the ball of the pen, under the shearing action of the pen's revolving ball. These new inks include at least one polyelectrolyte polymer; at least one highly polar solvent; colloidal silica; at least one low or medium polarity solvent having a dielectric constant at 25°C, of less than 35, and preferably less than 25; and other such ink ingredients as highly polar solvents, pigments, dyes, pH modifiers, pigment modifiers, thixotropy modifiers and surfactants.

The polyelectrolyte polymers have a number average molecular weight of at least 300,000, but preferably of at least 3,000,000. Examples of such polymers include Acrysol ASE 60, available from Rohm & Haas Company and Carbopol 934 available from B. F. Goodrich Company. Other polyelectrolyte polymers include polyethylene maleic anhydride EMA 91 and EMA 111, available from Monsanto Industrial Chemicals Company, and such polysaccharides as Keltone, Kelco-Gel, Xanthan gum, Keltrol and Kelzan, available from the Kelco Company. In our ink compositions, these polyelectrolyte polymers constitute about 1% to about 6% by weight, preferably about 2% by weight of the ink.

Supplements for the Carbopol 934 and Acrysol ASE 60 resins include polyvinyl methyl ethers such as Gantrez, available from GAF; and high molecular weight natural and synthetic rubber polymers. These supplements are not substitutes for the polyelectrolyte polymers, but can be added to our inks to improve their yield value, among other things.

The new inks must contain at least 5% by weight of one or more highly polar solvents, meaning solvents with dielectric constants at about 25% C, of greater than about 35. Among these highly polar solvents are water, methanol, glycol, glycerol, dimethylformamide, formamide, ethylene glycol and propylene glycol. The amount of highly polar solvent in our inks varies depending on the nature of the polyelectrolyte polymer, and on the nature and quantity of the other ink ingredients. However, such solvents can constitute from about 5% to about 65% by weight of the inks.

The new inks must also include at least one low polarity or medium polarity solvent having a dielectric constant of less than about 35. Such solvents include diethylene glycol; dipropylene glycol; ethylene glycol ethyl ether; ethylene glycol phenyl ether; tripropylene glycol methyl ether; toluene; polyglycols E300 and P 1200, available from Union Carbide Company and Dow Chemical Company, respectively; stearic acid; oleic acid and benzyl alcohol. These solvents are used in amounts that vary depending on the nature of the colloidal silica, and on the nature and relative amounts of the other ink constituents. Broadly, such solvents can constitute from about 1% to about 55% by weight of the inks.

The colloidal silicas in our inks include fumed silica or hydrated silica, and, in particular, the fumed silica sold under the tradename Cab-O-Sil M5 by Cabot Corporation. The quantity of colloidal silica in our inks should be in the range of about 1% to about 10% by weight of the ink composition.

Our inks may also include surfactants or wetting agents to promote hydrogen bonding of silicas. An example is Triton X100 available from Rohm & Haas Company. The quantity of surfactant used is in the range of about 0.2% to about 5% by weight of the ink composition.

Our inks may also include thixotropy modifiers such as polyglycols or resins in the amounts ranging from about 0.5% to about 10% by weight of the ink compositions. Examples of such modifiers are polyglycol P1200, available from Dow Chemical Company, polyglycols E200 and E300, available from Union Carbide, and Phtalopal L8587, available from B.A.S.F.

Our inks may also include pigments, pigment modifiers, dyes and pH modifiers. Pigments useful in our ink compositions are Cyan Blue BNF 55-3750, available from American Cyanamid; Bonadur Red 20-6440, available from American Cyanamid; Elftex 5 Carbon Black, available from Cabot Corporation; Chrome Yellow 40-4500, available from America Cyanamid; Mogul L Carbon Black, available from Cabot Corporation; and Methyl Violet MV 55-2919, available from American Cyanamid. Preferably,

such pigments are combined with protective pigment modifiers such as polyvinyl pyrrolidone K30. Pigments and pigment modifiers, where present, can constitute up to about 20% by weight of our inks.

Among the dyes useful in our ink compositions are Victoria Blue B.O. Base, available from American Cyanamid; Spirit Blue THN, available from American Cyanamid: Chrysoidine Y Base, available from American Cyanamid; Spirit Red 2G, available from American Cyanamid; Zapon Fast Fire Red B, available from B.A.S.F.; Spirit Yellow TG, available from American Cyanamid; Nigrosine base, available from American Cyanamid; Rhodamine base DY, available from American Cyanamid; and Spirit Orange 2G, available from American Cyanamid. Because the polyelectrolyte polymers are acidic, base dyes provide a means for neutralizing our ink compositions. Neutralization is essential to gelling our inks, which preferably have a pH in the range of about 6.7 to about 8. Where the nature or amount of the dyes is insufficient to form a gel, we can also use pH modifiers such as amines to neutralize the inks. Examples of such amines are diisopropanolamine, dodecylamine and Ethomeen C25 or di-orthotolylguanadine. Dyes, where present, constitute up to about 30% by weight of our inks.

To make our new ink compositions, we simply blend the ink constituents in the proper relative amounts in a blender until the desired gel forms. More preferably, we first combine the surfactants, solvents and thixotropy adjusters, then add the other constituents in the following order: Polyelectrolyte polymer; colloidal silicas; pigments and pigments modifiers, if any; dyes, if any; and pH modifiers, if any.

Our new ink compositions have substantial yield values when at rest, and tend to resist flow under the force of gravity or under the large pressures within the pressurized reservoirs of our pens. However, under the tremendous shearing forces of the revolving ball in the ball point, our inks drop in viscosity into the range of about 100 to about 4,000 centipoise.

For these pressurized roller pen inks the "Thixotropic Ratio" is higher than that of other ball-point pen inks, but, as measured by the following procedure, varies from a low of 10:1 to a high of 150:1. We determined a special "Thixotropic Ratio" by measuring the viscosity of the ink at 25 degree C with a spindle revolving at a slow speed of 0.5 revolutions per minute and comparing that with the viscosity of the same ink with the spindle revolving at a faster speed of 100 revolutions per minute. We used a Brookfield HBT Viscometer with a No. 6 or No. 7 spindle.

Our new inks also have sufficient adhesion and cohesion so that they adhere to the ball of the pen when the ball is revolving, yet transfer readily from the ball onto the writing surface.

Pressurized ball-point writing cartridges typically include a tubular, rigid ink reservoir with a ball-point structure joined to the lower end of the reservoir. The ball-point structure includes a writing ball mounted in a ball socket. The ink itself is fed into the reservoir, pressurized with an inert gas such as nitrogen, air or carbon dioxide to a pressure in excess of 1 to about 15 atmospheres, and then sealed to prevent escape of the gas from the reservoir. At rest, our inks are gels that do not ooze from the reservoir. Under the shearing force of the ball when the pen is in use, the viscosities of our inks become sufficiently low that the ball rotates easily in its socket and deposits an intense line of ink onto the writing surface.

Following our preferred formulation method, we prepared the following new inks, and then loaded them into pressurized cartridge ball-point pens. These ball-point pens have the ball and socket structure set forth at column 4, lines 32 and following, in U.S. Patent 3,425,779, which issued February 4, 1969.

In each cartridge, we used air or nitrogen as the pressurizing gas, and pressurized each cartridge to about 90 pounds per square inch.

We calculated the thixotropic ratio of each ink formulation from apparent viscosity measurements taken with the Brookfield HBT viscometer using a No. 6 or No. 7 spindle at about 25°C. These results appear in each example.

Example 1

Blue Ink

Constituents	*Percent by Weight*
Butyrolactone (GAF)	21.36
Propylene Glycol	18.90
Glycerine	9.70
Distilled Water	5.80
Surfactant Triton ×100 (Rohm & Haas)	0.48
Polyglycol P1200 (Dow)	1.94
Polyacrylic Resin Carbopol 934 (Goodrich)	1.94
Polyvinyl Pyrrolidone K30 (BASF)	2.91
Pigment Cyanblue BNF 55-3750 (Cyanamid)	3.92
Stearic Acid (Emery Co.)	3.92
Dye Victoria Blue B.O. Base (Cyanamid)	3.92
Dye Spirit Blue THN (Cyanamid)	16.50
Dye Calco Methyl Violet Base (Cyanamid)	5.80
Cab-O-Sil M5 Fumed Colloidal Silica (Cabot)	1.94
Di-o-tolylguanadine (DuPont)	0.97
	100.00

We tested the viscosities of this ink on a Brookfield HBT viscometer with a No. 6 spindle at 25°C, at the following rotation speeds (RPM) and obtained the following viscosities (CPS):

RPM	*Centipoises (CPS)*
0.5	2,960,000
1.0	1,640,000
2.5	816,000
5.0	416,000
10.0	200,000
20.0	128,000
50.0	48,000
100.0	30,400

Thixotropic ratio: 97:1

Example 2

Blue Ink

Constituents	*Percent by Weight*
Dimethylformamide	41.0
Glycerine	14.0
Distilled Water	6.0
Surfactant Triton ×100 (Rohm & Haas)	0.5
Polyglycol P1200 (Dow)	2.0
Polyacrylic Resin Carbopol 934 (Goodrich)	2.0
Polyvinyl Pyrrolidone PVP K30 (BASF)	3.0
Pigment Cyanblue BNF 55-3750 (Cyanamid)	6.0
Pigment Bonadur Red 20-6440	1.0
Stearic Acid (Emery Co.)	3.0
Dye Victoria Blue B.O. Base (Cyanamid)	2.5
Dye Methyl Violet Base DY (Cyanamid)	4.0
Dye Spirit Blue THN (Cyanamid)	13.0
Cab-O-Sil M5 (Cabot Co.)	2.0
	100.0

We tested the viscosities of this ink on a Brookfield HBT viscometer with a No. 6 spindle at 25°C, at the following rotation speeds (RPM) and obtained the following viscosities (CPS):

RPM	Centipoises (CPS)
0.5	512,000
1.0	352,000
2.5	188,800
5.0	115,200
10.0	71,200
20.0	44,200
50.0	23,000
100.0	14,750

Thixotropic ratio: 34.7:1

Example 3

Black Ink

Constituents	Percent by Weight
Dimethylformamide	42.0
Glycerine	13.0
Distilled Water	2.0
Surfactant Triton ×100 (Rohm & Haas)	0.5
Polyglycol E200 (Union Carbide)	2.0
Polyacrylic Acid Resin Carbopol 934 (Goodrich)	2.0
Polyvinyl Pyrrolidone K30 (BASF)	3.0
Carbon Black Elftex 5 (Cabot Corp.)	6.0
Pigment Cyanblue BNF 55-3750 (Cyanamid)	2.0
Pigment Bonadur Red 20-6440 (Cyanamid)	1.0
Pigment Chrome Yellow 40-4500 (Cyanamid)	0.5
Stearic Acid (Emery Co.)	4.0
Cab-O-Sil M5 (Cabot Co.)	3.0
Dye Calco Blue Base N (Cyanamid)	6.0
Dye Methyl Violet Base DY (Cyanamid)	6.0
Dye Chrysoidine Y Base (Cyanamid)	2.5
Dye Spirit Red 2G (Cyanamid)	3.0
Dye Spirit Yellow TG (Cyanamid)	1.5
	100.0

We tested the viscosities of this ink on a Brookfield HBT viscometer with a No. 7 spindle at 25°C, at the following rotation speeds (RPM) and obtained the following viscosities (CPS):

RPM	Centipoises (CPS)
0.5	1,360,000
1.0	928,000
2.5	550,400
5.0	345,400
10.0	218,400
20.0	141,600
50.0	67,840
100.0	45,920

Thixotropic ratio 29.6:1

Example 4

Black Ink

Constituents	Percent by Weight
Butyrolactone	40.7
Glycerine	13.0
Distilled Water	5.6
Surfactant Triton x100 (Rohm & Haas)	0.4
Polyglycol P1200 (Dow)	1.8
Polyacrylic Acid Resin Carbopol 934 (Goodrich)	1.8
Polyvinyl Pyrrolidone K30 (BASF)	1.8
Carbon Black Elftex 5 (Cabot Co.)	1.8
Carbon Black Mogul L (Cabot Co.)	1.8
Stearic Acid (Emery Co.)	2.8
Dye Calco Blue Base N (Cyanamid)	8.3
Dye Methyl Violet Base DY (Cyanamid)	8.3
Dye Chrysoidine Y Base (Cyanamid)	2.8
Dye Spirit Red 2G (Cyanamid)	3.7
Dye Spirit Yellow TG (Cyanamid)	1.8
Di-o-tolylguanadine (DuPont)	1.8
Cab-O-Sil M5	1.8
	100.0

We tested the viscosities of this ink on a Brookfield HBT viscometer with a No. 6 spindle at 25°C, at the following rotation speeds (RPM) and obtained the following viscosities (CPS):

RPM	Centipoises (CPS)
0.5	600,000
4.0	380,000
2.5	216,000
5.0	128,000
10.0	82,000
20.0	54,000
50.0	25,600
100.0	16,000

Thixotropic ratio: 37.5:1

Example 5

Black Ink

Constituents	Percent by Weight
N-Methyl-2-Pyrrolidone (GAF)	24.0
Benzyl Alcohol	20.0
Glycerine	6.0
Distilled Water	6.0
Surfactant Triton x100 (Rohm & Haas)	1.0
Polyglycol P1200 (Dow)	2.0
Polyacrylic Acid Resin Carbopol 934 (Goodrich)	2.0
Polyvinyl Pyrrolidone K30 (BASF)	3.0
Carbon Black Elftex 5 (Cabot Co.)	6.0
Pigment Methyl Violet MV 55-2919 (Cyanamid)	4.0
Cab-O-Sil M5 (Cabot Co.)	2.0
Stearic Acid (Emery Co.)	3.0
Dye Calco Blue Base N (Cyanamid)	6.0
Dye Methyl Violet Base DY (Cyanamid)	6.0
Dye Chrysoidine Y Base (Cyanamid)	2.5
Dye Spirit Red 2G (Cyanamid)	3.0
Dye Spirit Yellow TG (Cyanamid)	1.5
Dodecylamine Armeen 12 (Armour Chemical)	2.0
	100.0

We tested the viscosities of this ink on a Brookfield HBT viscometer with a No. 7 spindle at 25°C, at the following rotation speeds (RPM) and obtained the following viscosities (CPS):

RPM	*Centipoises (CPS)*
0.5	1,024,000
1.0	512,000
2.5	192,000
5.0	112,000
10.0	80,000
20.0	56,000
50.0	35,000
100.0	22,000

Thixotropic ratio: 46:1

Example 6

Red Ink

Constituents	*Percent by Weight*
Butyrolactone	29.0
Glycerine	9.0
Distilled Water	15.0
Surfactant Triton x100 (Rohm & Haas)	0.5
Polyglycol E200 (Union Carbide)	5.0
Polyacrylic Acid Resin Carbopol (Goodrich)	2.0
Polyvinyl Pyrrolidone K30 (BASF)	3.0
Pigment Bonadur Red 20-6440 (Cyanamid)	6.0
Cab-O-Sil M5 (Cabot)	2.0
Stearic Acid (Emery Co.)	3.0
Dye Spirit Red 2G (Cyanamid)	16.0
Dye Spirit Orange 2G (Cyanamid)	2.0
Dye Rhodamine Base DY (Cyanamid)	4.0
Di-o-tolylguanadine (DuPont)	1.0
Di-isopropanolamine (Union Carbide)	2.5
	100.0

We tested the viscosities of this ink on a Brookfield HBT viscometer with a No. 7 spindle at 25°C, at the following rotation speeds (RPM) and obtained the following viscosities (CPS):

RPM	*Centipoises (CPS)*
0.5	1,240,000
1.0	704,000
2.5	371,000
5.0	249,000
10.0	153,600
20.0	97,600
50.0	59,520
100.0	38,720

Thixotropic ratio: 32:1

Example 7

Black Ink

Constituents	*Percent by Weight*
Benzyl Alcohol	27.0
Diethylene Glycol	12.0
Glycerine U.S.P.	12.0
Distilled Water	4.0
Surfactant Triton x100 (Rohm & Haas)	0.5
Polyglycol E300 (Union Carbide)	2.0
Polyacrylic Acid Resin Carbopol 934 (Goodrich)	1.5
Saponifiable Resin Phtalopal L8587 (BASF)	3.0
Polyvinyl Pyrrolidone K90 (GAF)	0.5
Carbon Black Mogul L (Cabot Co.)	4.0
Stearic Acid (Emery Co.)	3.0
Cab-O-Sil M5 (Cabot Co.)	2.0
Dye Calco Blue Base N (Cyanamid)	8.0
Dye Methyl Violet Base DY (Cyanamid)	8.0
Dye Zapon Fast Fire Red B (BASF)	3.5
Dye Calco Chrysoidine Y Base (Cyanamid)	4.0
Dye Calco Nigrosine Base BPS (Cyanamid)	4.0
Di-o-tolylguanadine (DuPont)	1.0
	100.0

We tested the viscosities of this ink on a Brookfield HBT viscometer with a No. 7 spindle at 25°C, at the following rotation speeds (RPM) and obtained the following viscosities (CPS):

RPM	*Centipoises (CPS)*
0.5	512,000
1.0	400,000
2.5	224,000
5.0	156,600
10.0	104,000
20.0	70,000
50.0	44,800
100.0	30,400

Thixotropic ratio: 17:1

Example 8

Black Ink

Constituents	*Percent by Weight*
Methanol	17.9
Butyrolactone	32.2
Glycerine	9.3
Distilled Water	2.2
Surfactant Triton x100 (Rohm & Haas)	0.8
Polyglycol P1200 (Dow)	1.5
Pigment Cyanblue BNF 55-3750 (Cyanamid)	2.9
Pigment Bonadur Red 20-6440	1.5
Carbon Black Elftex 5 (Cabot Co.)	4.3
Polyvinyl Pyrrolidone K30 (BASF)	2.2
Stearic Acid (Emery Co.)	2.9
Dye Calco Blue Base N (Cyanamid)	3.6
Dye Calco Methyl Violet Base DY (Cyanamid)	3.6
Dye Calco Chrysoidine Y Base	1.5
Dye Spirit Red 2G	1.8
Dye Spirit Yellow TG	0.4
Acrysol ASE 60 (Rohm & Haas)	5.0
Cab-O-Sil M5 (Cabot Co.)	5.0
Di-o-tolylguanadine	1.4
	100.0

We tested the viscosities of this ink on a Brookfield HBT viscometer with a No. 6 spindle at 25°C, at the following rotation speeds (RPM) and obtained the following viscosities (CPS):

RPM	*Centipoises (CPS)*
0.5	720,000
1.0	320,000
2.5	144,000
5.0	80,000
10.0	44,000
20.0	26,000
50.0	12,000
100.0	6,800

Thixotropic ratio: 106:1

Example 9

Black Ink

Constituents	*Percent by Weight*
Diethylene Glycol	28.0
Benzyl Alcohol	15.0
Glycerine	10.0
Distilled Water	4.0
Triton x100 (Rohm & Haas)	0.5
Polyglycol E300 (Union Carbide)	2.0
Polyacrylic Acid Resin Carbopol 934 (Goodrich)	2.0
Stearic Acid	3.0
Carbon Black Elftex 5 (Cabot Co.)	4.0
Polyvinyl Pyrrolidone K30 (BASF)	2.0
Di-o-tolylguanadine	1.0
Dye Calco Blue Base N (Cyanamid)	8.4
Dye Calco Methyl Violet Base DY (Cyanamid)	8.4
Dye Calco Nigrosine Base BPS	1.4
Dye Calco Chrysoidine Y Base	4.4
Dye Zapon Fast Fire Red B (BASF)	3.4
Hi-Sil T-600 (PPG Industries, Inc.)	2.0
Di-isopropanolamine	0.5
	100.0

We tested the viscosities of this ink on a Brookfield HBT viscometer with a No. 6 spindle at 26°C, at the following rotation speeds (RPM) and obtained the following viscosities (CPS):

RPM	*Centipoises (CPS)*
0.5	352,000
1.0	224,000
2.5	184,000
5.0	96,000
10.0	60,000
20.0	36,000
50.0	18,000
100.0	9,600

Thixotropic ratio: 36:1

Example 10

Black Ink

Constituents	*Percent by Weight*
Dimethylformamide	30.0
Benzyl Alcohol	11.5
Glycerine	11.5
Diethylene Glycol	2.0
Surfactant Triton ×100	0.5
Polyglycol P1200	2.0
Polyacrylic Acid Resin Carbopol 934	2.5
Stearic Acid	2.8
Polyvinyl Pyrrolidone K30	2.0
Carbon Black Elftex 5	3.8
Carbon Black Mogul L	1.75
Dye Calco Blue Base N	7.75
Dye Calco Methyl Violet Base DY	7.75
Dye Calco Chrysoidine Y Base	4.2
Dye Calco Nigrosine Base BPS	3.75
Dye Zapon Fast Fire Red B	3.2
Cab-O-Sil M5	2.0
Di-o-tolylguanadine	1.0
	100.00

We tested the viscosities of this ink on a Brookfield HBT viscometer with a No.6 spindle at 26°C, at the following rotation speeds (RPM) and obtained the following viscosities (CPS):

RPM	*Centipoises (CPS)*
0.5	760,000
1.0	480,000
2.5	256,000
5.0	152,000
10.0	90,000
20.0	52,000
50.0	26,400
100.0	14,800

Thixotropic ratio: 51:1

Claims

1. A ball-point marking instrument including a sealed marking fluid reservoir having a socket located at one end thereof; a ball rotatably mounted within said socket so as to extend into the interior of and to the exterior of said reservoir; a marking fluid within said fluid reservoir in contact with said ball; a charge of pressurized gas within said reservoir at the extremity remote from the socket, said pressurized gas serving to force said marking fluid against said ball; said marking fluid comprising at least one polyelectrolyte polymer; at least about 5% by weight of at least one solvent of high polarity;

at least one solvent of low or medium polarity; about 1% to about 10% colloidal silica; and at least one coloring agent.

2. The ball-point marking instrument of claim 1 wherein said highly polar solvent is water.

3. The ball-point marking instrument of claim 1 or claim 2 wherein the marking fluid further comprises at least one member selected from the group consisting of pH modifiers, pigment modifiers, thixotropy modifiers and surfactants.

4. The marking instrument of any one of claims 1, 2 or 3 wherein said marking fluid has a thixotropic ratio in the range of about 10:1 to about 150:1 measured on the Brookfield HBT viscometer at 25°C, using a No. 6 or No. 7 spindle.

5. An ink composition comprising at least one polyelectrolyte polymer; water; at least one solvent of low or medium polarity; at least one colloidal silica; and at least one coloring agent.

6. The ink composition of claim 5 including at least one highly polar solvent.

7. The ink composition of claim 5 or 6 wherein the ink composition further comprises at least one member selected from the group consisting of pH modifiers, pigment modifiers, thixotropy modifiers and surfactants.

8. The ink composition of any one of claims 5 or 6 wherein said ink composition has a thixotropic ratio in the range of about 10:1 to about 150:1 measured on the Brookfield HBT viscometer at 25°C, using a No. 6 or No. 7 spindle.

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